

CONCLUSION

The potentiometer set-up here described has proved to be convenient for the laboratory.

The writer has experienced no difficulty from stray currents in about 10 months' operation. Although the danger of trouble from this source is apparently no greater with this

arrangement than with the usual circuits, if the proper set-up is made, nevertheless, a little extra care in arranging these circuits will without doubt be worth while.

The arrangement might be of service for regulating the terminal voltages of commercial recording potentiometers in factories where it is now the custom to employ dry cells.

Analysis of Naphthalenesulfonic Acids and Naphthalene¹ Supplementary Report

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IN A recent paper by the authors upon the "Analysis of Naphthalenesulfonic Acids and Naphthalene,"² the detailed procedure of analysis and preparation of reagents for the analysis of naphthalenesulfonic acids was accidentally omitted when the article was printed. The methods, which consist in determining the naphthalene carbon present by oxidation of the naphthalene residue to phthalic anhydride, and the sulfonic acid sulfur present by isolation of the soluble barium sulfonates with subsequent gravimetric determinations of barium, are given here.

REAGENTS

VANADIC ACID SOLUTION—To prepare 1 liter of the oxidizing solution, transfer 63 grams of pure ammonium metavanadate (NH_4VO_3) to a 2.5-liter beaker and add 220 cc. of distilled water. To this mixture add gradually with agitation 780 cc. of concentrated sulfuric acid. Cool the solution to room temperature and preserve it in a glass-stoppered bottle.

BARIUM CARBONATE—The barium carbonate used in this determination of sulfonic acid sulfur must be free from all soluble salts. Satisfactory material may be obtained by boiling 200 to 300 grams of pure precipitated barium carbonate with 1 liter of distilled water, filtering, and washing the barium carbonate with hot water.

ANALYTICAL PROCEDURE

DETERMINATION OF NAPHTHALENE CARBON (C_{10})—If sulfites are present in the sample it should be first boiled in acid solution to eliminate SO_2 . Pipet a 25-cc. aliquot of the sample containing 0.25 to 0.30 gram of the naphthalenesulfonic acid into a 200-cc. Erlenmeyer flask and add at room temperature 90 cc. of the vanadic acid reagent. Insert a thermometer in the flask and heat the mixture to 120°C . in not less than 10 minutes. Maintain the temperature of the oxidation at $120^\circ\text{C} \pm 2^\circ$ for exactly 15 minutes, then immediately pour the solution into 200 cc. of cold water in a 750-cc. Erlenmeyer flask. Rinse the small Erlenmeyer with cold water, cool the drowned mixture to room temperature, then transfer it to a 500-cc. volumetric flask and dilute to the mark with distilled water.

Titrate 150-cc. aliquots of the solution in 200 cc. of water at 70° to 80°C . with 0.1 *N* permanganate solution. The permanganate may be run in rapidly until the solution changes in color from green to greenish yellow. Then add the permanganate in 2 to 3-drop portions until an end point permanent for 20 seconds is obtained.

A blank determination should be run upon the oxidizing solution using 25 cc. of distilled water in place of the sample

aliquot. Reagent made from good quality ammonium metavanadate will have a blank of not more than 1.0 cc. of 0.1 *N* permanganate.

Calculation:

$$\frac{(\text{Cc. KMnO}_4 - \text{blank}) \times \text{normality of KMnO}_4 \times 0.667}{\text{Weight of sample in aliquot titrated}} = \text{Per cent naphthalene carbon}$$

DETERMINATION OF SULFONIC ACID SULFUR—Pipet a 100-cc. aliquot of the sample (having the same concentration as the aliquot used for the naphthalene carbon determination) into a 1-liter beaker, add 400 cc. of hot distilled water and 5 grams of washed barium carbonate. Cover the beaker and boil the mixture for 30 to 40 minutes, then filter off the barium sulfate and excess carbonate and wash the cake with cold water. Dilute the filtrate and washings to 800 cc. in a liter beaker, heat to boiling, and precipitate the barium by adding 40 cc. of 5 per cent sulfuric acid (by volume). Digest the solution until precipitation is complete, then filter off, ignite, and weigh the barium sulfate.

Run a blank determination on the barium carbonate using 5 grams of the carbonate and 500 cc. of distilled water. Treat this determination exactly like the determination of the sample.

Calculation:

$$\frac{(\text{Weight of BaSO}_4 - \text{blank}) \times 27.47}{\text{Weight of sample in aliquot}} = \text{Per cent sulfonic acid sulfur}$$

The degree of sulfonation is then expressed by the following formula, where a result of 1.00 indicates monosulfonation, 2.00 complete disulfonation, and 3.00 complete trisulfonation.

$$\frac{3.745 \times \text{per cent sulfonic acid sulfur}}{\text{Per cent naphthalene carbon}} = \text{Degree of sulfonation}$$

DISCUSSION OF THE ANALYTICAL PROCEDURE

The procedure for naphthalene carbon applied to ordinary mixtures of sulfonic acids is considered accurate within 1 per cent of the amount present. The analysis is open to the objection that other oxidizable material present will be determined and calculated as naphthalene carbon. In practice, however, this objection has been found more theoretical than actual; the conditions of temperature and high concentration of oleum in the process of sulfonation operate to eliminate easily oxidizable organic materials, and it should be noted in this respect that each mol of naphthalene residue requires 18 equivalents of oxygen, a ratio which causes the presence of inorganic oxidizable impurities to introduce relatively small errors.

The analysis for degree of sulfonation where the estimation of sulfonic acid sulfur is included is considered accurate within 2 per cent. This method is not applicable to the salts of the sulfonic acids or to mixtures containing salts such as sodium sulfate.

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² THIS JOURNAL, 16, 27 (1924).